

1-913
p.32

**FINAL REPORT ON
THERMAL MODELING OF A Ni-H₂
BATTERY CELL**

for

NASA Grant NCC 3-69

by

Si-Ok Ryu

K. J. De Witt

T. G. Keith

**DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF TOLEDO**

(NASA-GP-108931) THERMAL MODELING OF A
Ni-H₂ BATTERY CELL Final Technical Report
(Toledo Univ.) 37 p. OCT 09A

NR1-25319

G3
44/33 Unclass
001931

CONTENTS

	<u>PAGE</u>
I. INTRODUCTION	1
II. GENERAL Ni-H ₂ IPV CELL DESIGN	2
1. Ni-H ₂ IPV CELL STRUCTURE	2
A. ELECTRODE STACK ASSEMBLY	2
B. PRESSURE VESSEL	6
C. ASSOCIATED SUPPORT HARDWARE	6
2. ELECTROCHEMICAL REACTIONS WITHIN THE CELL	8
A. NORMAL OPERATION	8
B. OVERCHARGE	9
C. REVERSAL	9
III. ELECTRODE STACK DESIGN	12
1. AIR FORCE/HUGHES DESIGN	12
2. ADVANCED DESIGNS	12
IV. THERMAL DESIGN	16
1. HEAT GENERATION	17
2. THERMAL MODELING	18
V. RESULTS AND DISCUSSION	22

I. INTRODUCTION

The nickel-hydrogen secondary battery has many desirable features which make it attractive for satellite power systems. It can provide a significant improvement over the energy density of present spacecraft nickel-cadmium batteries, combined with longer life, tolerance to overcharge and possibility of state-of-charge indication. However, to realize these advantages, accurate thermal modeling of nickel-hydrogen cells is required in order to properly design the battery pack so that it operates within a specified temperature range during the operation. Maintenance of a low operating temperature and a uniform temperature profile within the cell will yield better reliability, improved cycle life and better charge/discharge efficiencies.

This research has the objective of developing and testing a thermal model which can be used to characterize battery operation. Primarily, temperature distribution with the heat generation rates as a function of position and time will be evaluated for a Ni-H₂ cell in the three operating modes: 1) charge cycle 2) discharge cycle and 3) overcharge condition, if applicable. Variables to be examined will include charging current, discharge rates, state of charge, pressure and temperature. Once the thermal model has been developed, this resulting model will predict the actual operating temperature and temperature gradient for the specific cell geometry to be used.

II. GENERAL Ni-H₂ IPV CELL DESIGN

Ni-H₂ batteries consist of several series-connected individual pressure vessel (IPV) cells for the purpose of increasing voltage or energy capacity. These are designed to contain hydrogen gas under pressure within the shells. Basic components of the Ni-H₂ IPV cell are the electrode stack assembly, the cylindrical pressure vessel with hemispherical end domes, and the associated support hardware. Figure 1. shows a typical baseline Ni-H₂ IPV cell structure [1,2]. The electrode stack assembly is mounted on a central core between two rigid end plates. Tabs from each electrode are attached to electrical terminals which are located on each end of the cell.

1. Ni-H₂ IPV CELL STRUCTURE

A. ELECTRODE STACK ASSEMBLY

The electrode stack assembly consists of repeating units of positive (nickel) electrodes, separators, negative (hydrogen) electrodes, and gas screens assembled in a cylindrical pressure vessel. These repeating units are connected in series to achieve the desired capacity. They are shaped in a pineapple slice pattern. The separators are extended beyond the electrodes to contact the pressure vessel for the electrolyte recycling.

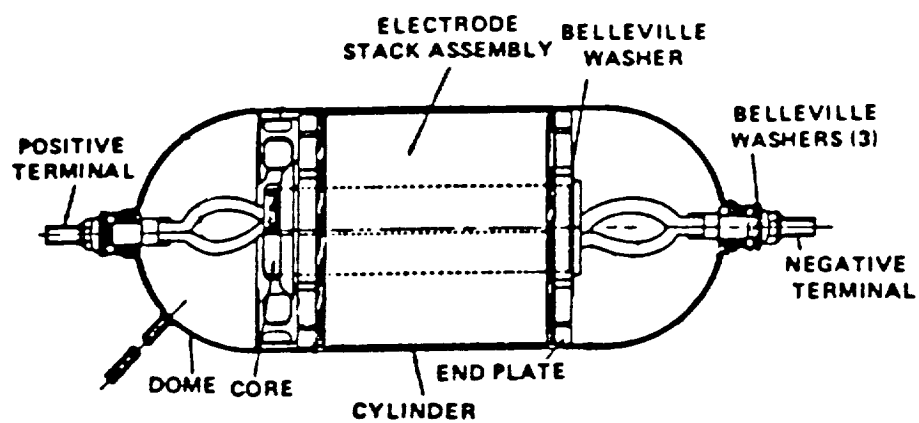


FIGURE1. IPV CELL ASSEMBLY

[POSITIVE ELECTRODE]

The positive electrodes are fabricated by the electrochemical impregnation of plaque with nickel hydrogen $[\text{Ni}(\text{OH})_2]$ active material onto a nickel screen substrate.

[NEGATIVE ELECTRODE]

The negative electrodes are fabricated by screening a platinum-teflon mixture onto a photochem-etched, teflon backed nickel substrate, followed by sintering.

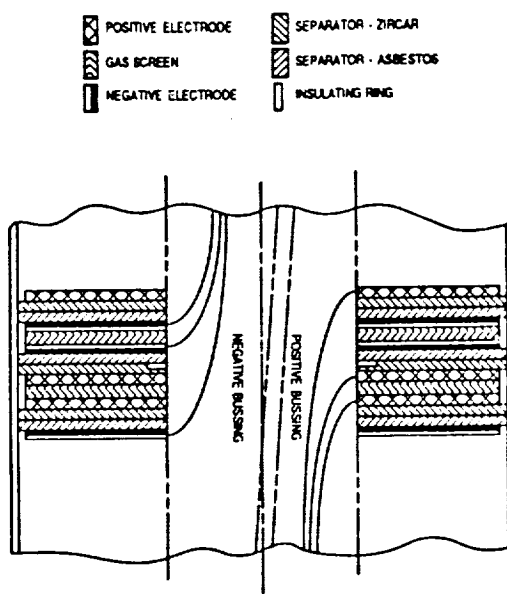
[SEPARATOR]

The separator plate prevents direct contact between the negative and the positive electrodes and acts as a reservoir for the electrolyte. A dual separator, consisting of one layer of asbestos and one layer of zircar, is used [3]. The edges of the separator are serrated to facilitate gas movement inside the wall and are in contact with the wall wick on the inner surface of the pressure vessel for the electrolyte recycling. The electrolyte is a 31 percent aqueous solution of potassium hydroxide.

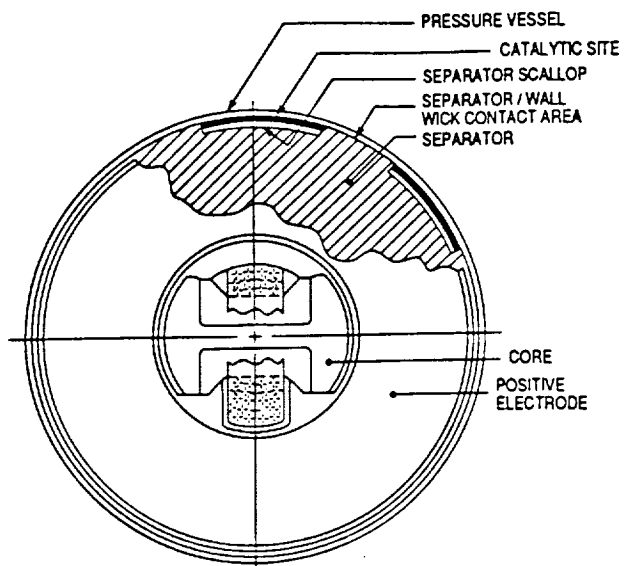
[GAS SCREEN]

Hydrogen gas is transported directly across the gas screens between the positive and negative electrodes. The gas screens are made of polypropylene.

Figure 2. illustrates the stack arrangement of an advanced cell [4]. This cell design features (1) the back-to-back stack configuration, (2) the use



a) STACK ARRANGEMENT



b) CELL STACK CROSS SECTION

FIGURE 2. IPV CELL STACK CONFIGURATION

of catalytic sites on the wall for the thermal management, and (3) the use of serrated edge separators to facilitate hydrogen gas movement within the cell while still maintaining physical contact with the cell stack.

B. PRESSURE VESSEL

The cylindrical pressure vessel is made of Inconel 718 and coated with zirconium oxide, which serves as a wall wick, on the inner surface of the vessel. The zirconium oxide liner and separators provide for electrolyte recirculating to the stack due to loss either by evaporation or recombination differences within the cell [5].

C. ASSOCIATED SUPPORT HARDWARE

The central core provides the radial mechanical support for the cell stack. The core is slotted for feed-through of electrical power leads from all positive and negative electrodes and is made from polysulfone, a thermoplastic with a high electrical resistivity, excellent mechanical strength, and stability. The end-plates serve to axially support the cell stack and provide uniform loads.

The design features of the IPV Ni-H₂ cell are summarized in Table 1.

TABLE 1 - CELL FEATURES**[MECHANICAL FEATURES]**

Pressure vessel	Thin walled, cylindrical with spherical ends Zirconium oxide coating on the inner surface Inconel 718
Stack	Cylindrical pineapple slice contained within pressure vessel
Stack support system	Central core, endplates, and Belleville washer
Terminal location	One at either end along cell centerline

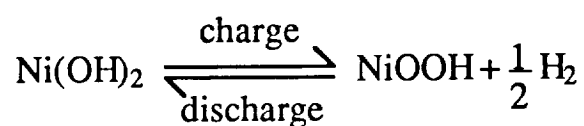
[ELECTROCHEMICAL FEATURES]

Negative electrode	Photochem-etched nickel substrate Teflon porous membrane and Pt catalyst
Positive electrode	Nickel screen substrate Ni(OH) ₂ active material with sintered carbonyl nickel powder plaque
Separator	Asbestos and zirconium oxide
Gas screen	Monofilament polypropylene screen
Electrolyte	31 percent KOH (aqueous)

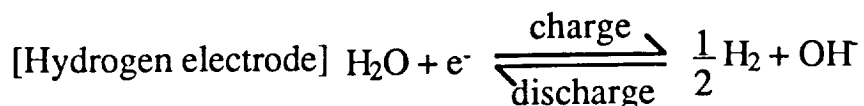
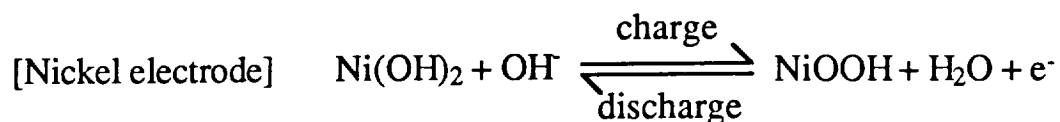
2. ELECTROCHEMICAL REACTIONS WITHIN THE CELL

A. NORMAL OPERATION

The overall electrochemical reaction within the cell is simple:

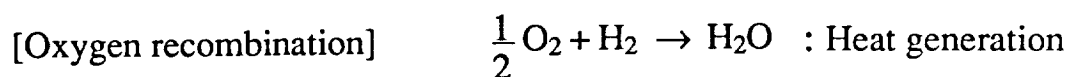
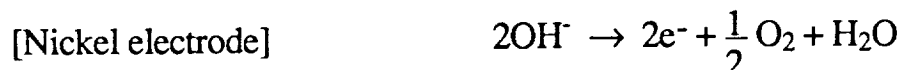


However, the generation and migration of water in the cell must be considered. The active nickel is converted from one valence state to another at the positive electrode. At the negative electrode, hydrogen gas is liberated from water by electrolysis during the charge cycle and is oxidized to water during discharge.



B. OVERCHARGE

During overcharge, the positive electrode has exhausted the Ni(OH)_2 active material and electrolysis occurs with oxygen generated at the positive electrode and with hydrogen at the negative electrode. The oxygen migrates to the negative electrode and chemically recombines with hydrogen to form water. This oxygen recombination leads to the waste heat generation during a charge/discharge cycle [6]. There is no change in the concentration of electrolyte (31% KOH) or the amount of water in the cell with continuous overcharge.

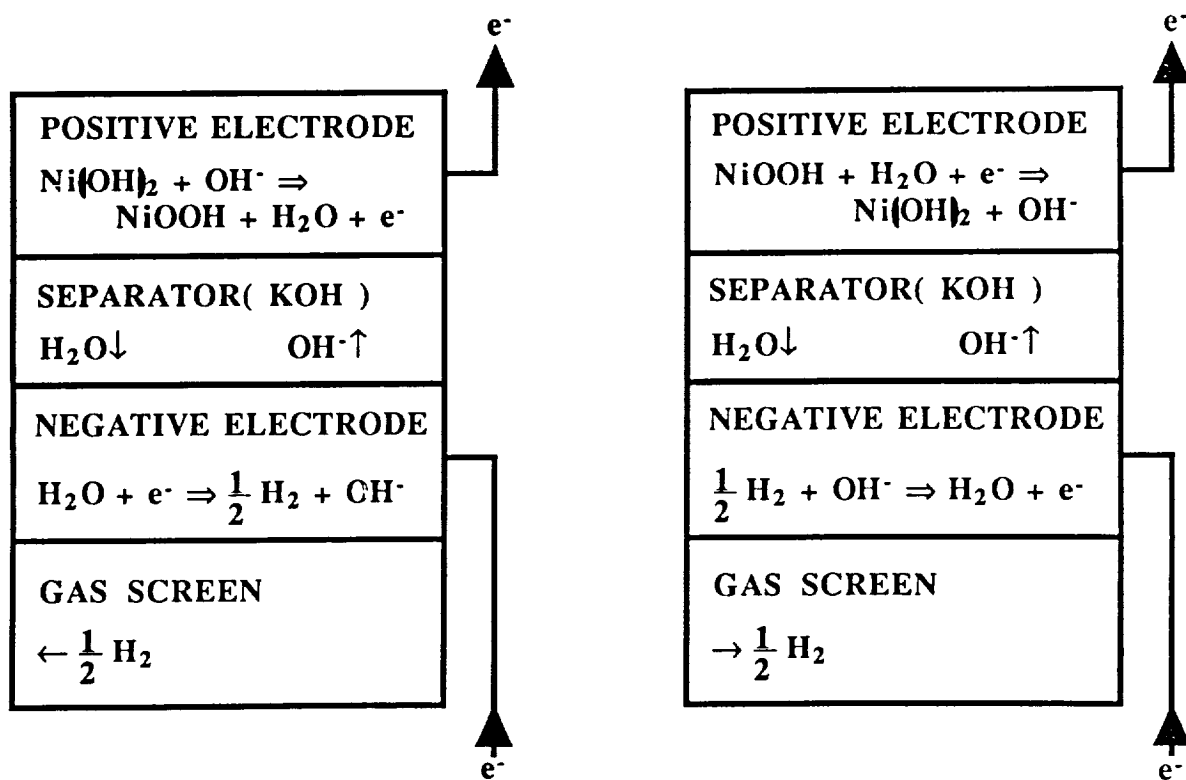


C. REVERSAL

During the cell reversal, hydrogen is generated at the positive electrode and consumed at the negative electrode at the same rate. Therefore, the cell can be continuously operated in the cell reversal mode without pressure buildup or net change in electrolyte concentration.



Figure 3. illustrates a simplified representation of the electrochemical reactions of one repeating unit of a Ni-H₂ cell [2].

FIGURE 3. Ni-H₂ CELL ELECTROCHEMICAL REACTIONS

III. ELECTRODE STACK DESIGN

There are three different designs for the electrode stack: the Air Force/Hughes design and two advanced designs. Figure 4. shows a schematic of each design [7].

1. AIR FORCE/HUGHES DESIGN

In the Air Force/Hughes design, electrodes of different types directly face each other. The nickel electrode is isolated from the adjacent hydrogen electrodes by a gas screen on one side and by a separator on the other. This allows recombination of oxygen, which is generated during overcharge, directly on the catalyzed hydrogen electrode surface through the gas screen to form water. Since this chemical reaction is very exothermic, a rapid recombination reaction, popping, can result in sintering of the catalyzed surface and/or local melting of the Teflon/catalyzed agglomeration due to excessive heating.

2. ADVANCED DESIGNS

Two different advanced IPV Ni-H₂ cell designs have been developed. One is referred to as the oxygen recombination capsule design and the other as the catalyzed wall wick design. The nickel electrodes, hydrogen electrodes, gas screen, pressure vessel, and electrolyte are identical to the

ones used in Air Force cells, but differ from each other and the Air Force design in the methods of oxygen recombination. Both alternatives are designed to prevent the oxygen from directly recombining at the hydrogen electrode. Other modified features in the advanced designs are the use of the serrated edge separators and the back-to-back electrode arrangement.

[OXYGEN RECOMBINATION CAPSULES]

An improved method of oxygen management is to use oxygen recombination capsules between the back-to-back nickel electrodes. In this design the oxygen produced on charge is diffused directly to the catalyzed recombination sites which are placed between the positive electrodes. This assures that the oxygen recombines at the alternative site rather than at the hydrogen electrode [7]. The water produced within the capsule will return to the nickel electrodes in vapor form. This method of oxygen management benefits the overall electrolyte management scheme, and helps prevent damage to the hydrogen electrode.

[CATALYZED WALL WICK]

Another method of oxygen recombination is to use a catalyzed wall wick. In this design, oxygen evolved in the nickel electrode during charge diffuses directly to the wall and recombines with hydrogen on the surface of the catalyzed wall wick. The catalyzed wall wick is fabricated by first depositing a thin zirconium oxide layer of wicking material on the

inner surface of the pressure vessel, as in the case of the Air Force design. A platinum Teflon mixture is coated in stripes onto the zirconium oxide surface. The water formed will return to the stack by means of the wall wick and separators. The advantages of using a catalyzed wall wick are thermal management as the heat of oxygen recombination is generated on the pressure vessel wall rather than at the hydrogen electrodes in the stack. By guiding the oxygen to recombine with hydrogen at the wall during overcharge, the localized heat generated during rapid recombination is readily dissipated. The hydrogen electrode is therefore prevented from any possible catalyst sintering.

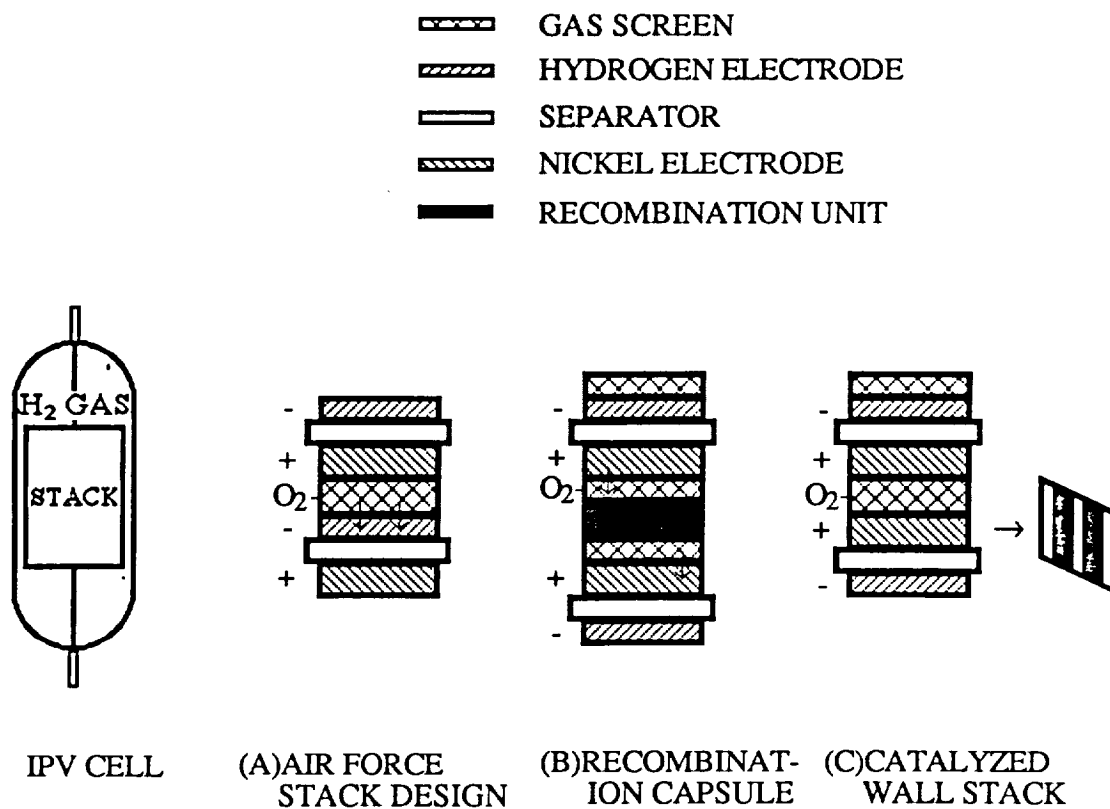


FIGURE 4. IPV STACK DESIGN CONFIGURATION

IV. THERMAL DESIGN

Thermal control of the battery is of particular concern to overall battery performance and life. The Nickel-Hydrogen battery cell should operate at a relatively low temperature with only a small temperature variation between the stack and the pressure vessel walls since a passive cooling system is used in the IPV cells. However, high energy is released by the reaction of oxygen recombination at the hydrogen electrode. This reaction occurs during the charge/overcharge cycle. A lack of adequate heat removal and uniform temperature distribution can cause maldistribution of the electrolyte solution due to evaporation or freezing, uneven current densities, local differences in charge/discharge efficiency, and the loss of platinum catalyst on the hydrogen electrode. If the temperature gradient within a Nickel-Hydrogen cell exceeds a critical value, the water in the electrolyte will evaporate from the hot stack and condense on the cooler pressure vessel walls. The maximum temperature gradient between the electrode stack and the vessel wall should never exceed 10 °C [8,9] in order to avoid water loss from the stack by evaporation. This undesirable water vapor transport causes electrolyte maldistribution. In addition, failure to maintain uniform heat distribution throughout a Ni-H₂ cell can lead to uneven current densities and local differences in charge/discharge efficiency. Poor current distribution coupled with oxygen recombination can lead to a hot spot on the negative electrode, resulting in physical damage such as local

sintering of the platinum catalyst and destruction of the cell through a rapid and uncontrolled reaction. This can also lead to an internal short circuit through local melting or drying of the separator and softening of the gas screens [9].

All of these problems will contribute to decreasing cell life and performance. Hence, proper thermal control is required in order to achieve long cycle life and improved charge/discharge efficiencies.

1. HEAT GENERATION

Heat generation will be expected in the cell during a charge/discharge cycle. The sources of the waste heat generation during the cycles are the oxygen recombination and the active material reactions. The oxygen recombination reaction is highly exothermic and it occurs mostly during overcharge on the negative electrode. The instantaneous power (the product of discharge current and thermal neutral voltage) is the only significant source of heat generation during discharge.

Mathematical expressions for the heat dissipation rate have been established in terms of current and voltage [7,10]. It is assumed that the rate of heat generation due to oxygen recombination is equivalent to the instantaneous rate of oxygen formation, and enthalpy changes of the stored hydrogen are disregarded. These expressions are

$$[\text{on charge}] \quad Q_C = - (I_c - I_e) (E_H - V) + I_e V$$

[on discharge] a constant (time average) heat load is assumed;

$$Q_D = - I_d (E_H - V)$$

where Q : instantaneous heat generation rate in W

I_c : total charge current in A

I_e : current used for oxygen generation in A

I_d : discharge current in A

V : operating voltage, $V_{avg} = 1.2V$

E_H : thermoneutral voltage, 1.51V

2. THERMAL MODELING

The transient heat transfer of the cylindrical Ni-H₂ IPV cell has been investigated in order to find the temperature distribution in the cell with the heat generation as a function of position and time. The Air Force stack design was chosen for the model geometry. Heat transfer between the stack and the pressure vessel wall is by conduction, radiation, and to a small extent by the natural convection of the hydrogen gas. A pseudo forced convection exists by virtue of the hydrogen gas generated or absorbed. However, to simplify the initial thermal modeling, several assumptions are made:

- 1) The properties for each component are assumed to be the same in both the radial and the axial directions.
- 2) In the cylindrical stacked disc construction, $T = T(r,z,t)$, since it is axi-symmetric.
- 3) The outside of the pressure vessel is assumed to be kept at a constant temperature.
- 4) The convective term in the cell is neglected since its effect on the total thermal performance is taken to be minimal, and all heat transfer is assumed to be by conduction.

[GOVERNING EQUATION]

Since the flow term is neglected in the cell, the governing differential equation for the temperature distribution in the cell is the energy equation:

$$\rho \hat{C}_v \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r \left(k \frac{\partial T}{\partial r} \right) \right] + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + Q$$

where $T \equiv T(t,r,z)$

$$Q \begin{cases} Q_C \equiv Q_C(t, \text{position}) \approx Q_C(t) : \text{on charge} \\ Q_D \equiv \text{Time Avg. Value} : \text{on discharge} \end{cases}$$

$$k \equiv k(T) \approx \text{constant}$$

[BOUNDARY CONDITIONS]

$$\text{I.C) } T=T_0 \text{ at } t=0$$

$$\text{BC 1) } -k \frac{\partial T}{\partial r} = h_1 (T - T_0) \text{ at } r = R_0 (\text{outside radius of stack})$$

$$\text{BC 2) } q_r = -k \frac{\partial T}{\partial r} = 0 \text{ at } r = 0$$

$$\text{BC 3) } -k \frac{\partial T}{\partial z} = h_2 (T - T_0) \text{ at } z = L_1$$

$$\text{BC 4) } -k \frac{\partial T}{\partial z} = h_3 (T - T_0) \text{ at } z = L_2$$

The heat generation rate can be calculated using the given equations. The thermal analysis in the cell may be classified into several domains. Figure 5. illustrates the domains of a single repeating unit of the cell stack for thermal analysis. The values of model geometry and the material properties of cell components are found in the Reference [10].

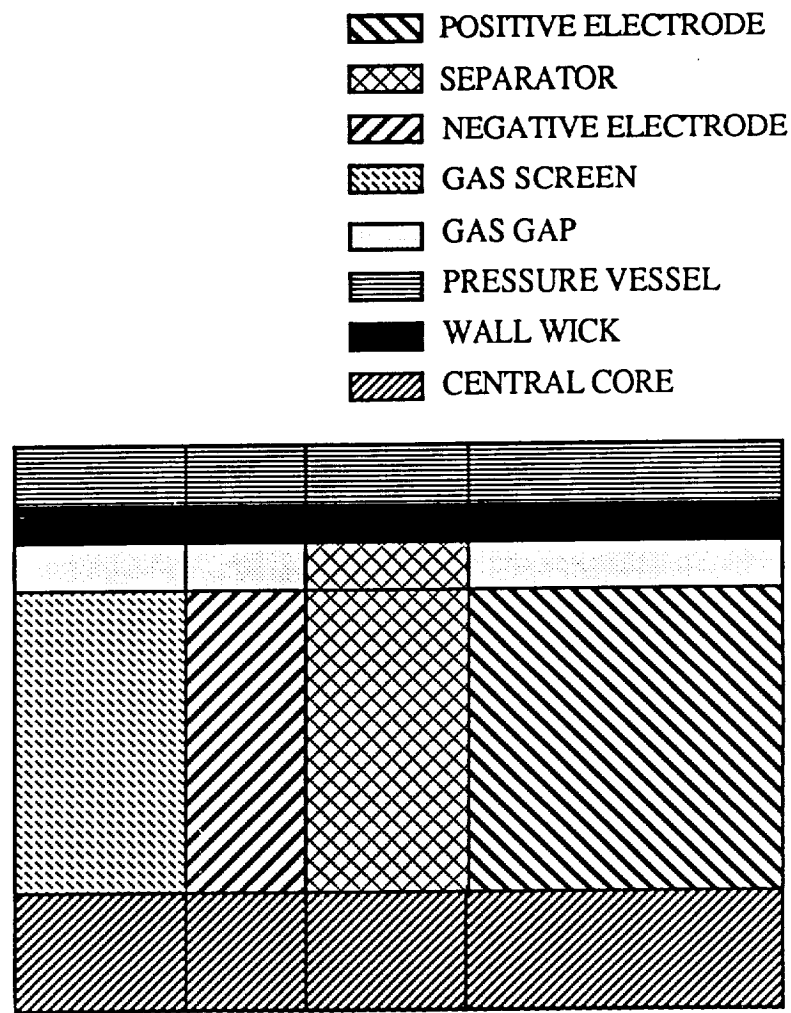


FIGURE 5. DOMAINS FOR THERMAL ANALYSIS

V. RESULTS AND DISCUSSION

Numerical results were obtained for unsteady, two-dimensional heat transfer in the cell. A finite element technique is employed to numerically solve the unsteady energy equation. As assumed, the hydrogen gas movement in the cell is neglected and the outside temperature of the cell is kept at 10 °C. Due to the symmetry, only one-half of the system is treated. The Finite element mesh for our model is illustrated in Figure 6.

As an example, only one cycle was simulated to determine the temperature profiles in the cell. Figure 7. represents the temperature contours for one repeating unit of the cell stack. Figure 8. shows the visualized photocopy taken for the time history of the temperatures at several nodes. For our Ni-H₂ IPV cell model, one charge/discharge cycle duration including a 1 to 2 hour discharge/charge interval of each cycle is 6 hours. However, since no waste heat is generated during the first 75 percent of charge, the first 2 hours are not shown here. The results illustrate that the temperature in the Air Force design increases sharply at the end of charge.

The temperature transient at the inside diameter of the nickel electrode is plotted in Figure 9. Temperature behavior at three different positions of the electrode are illustrated in Figure 10. As the figures show, the highest temperature is located at the inner diameter of the electrode. The temperature difference from the inner to the outer diameter of the electrode is approximately 10 °C. These results show reasonably good agreement with the results in Reference [7].

The finite element program is working well. If additional funding becomes available, the following work would be pursued:

1. Parameter study of performance of various cell designs;
2. More detailed heat source expressions incorporated;
3. Model extended to include H_2 convections;
4. Comparison of predicted results with experimental data.

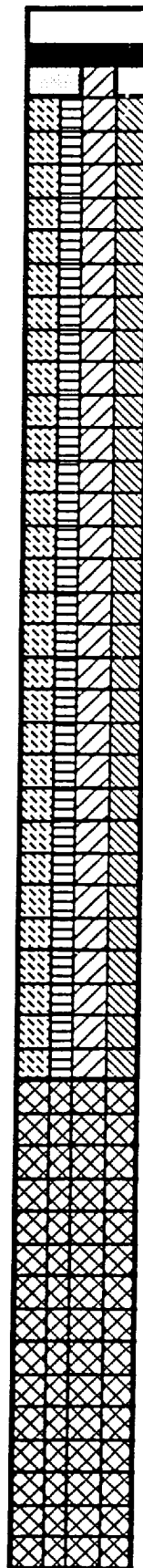
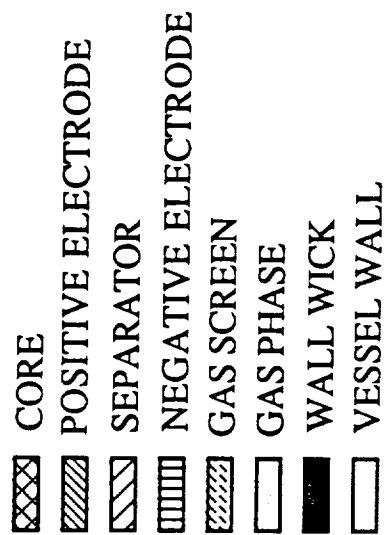


FIGURE 6. FINITE ELEMENT MESH

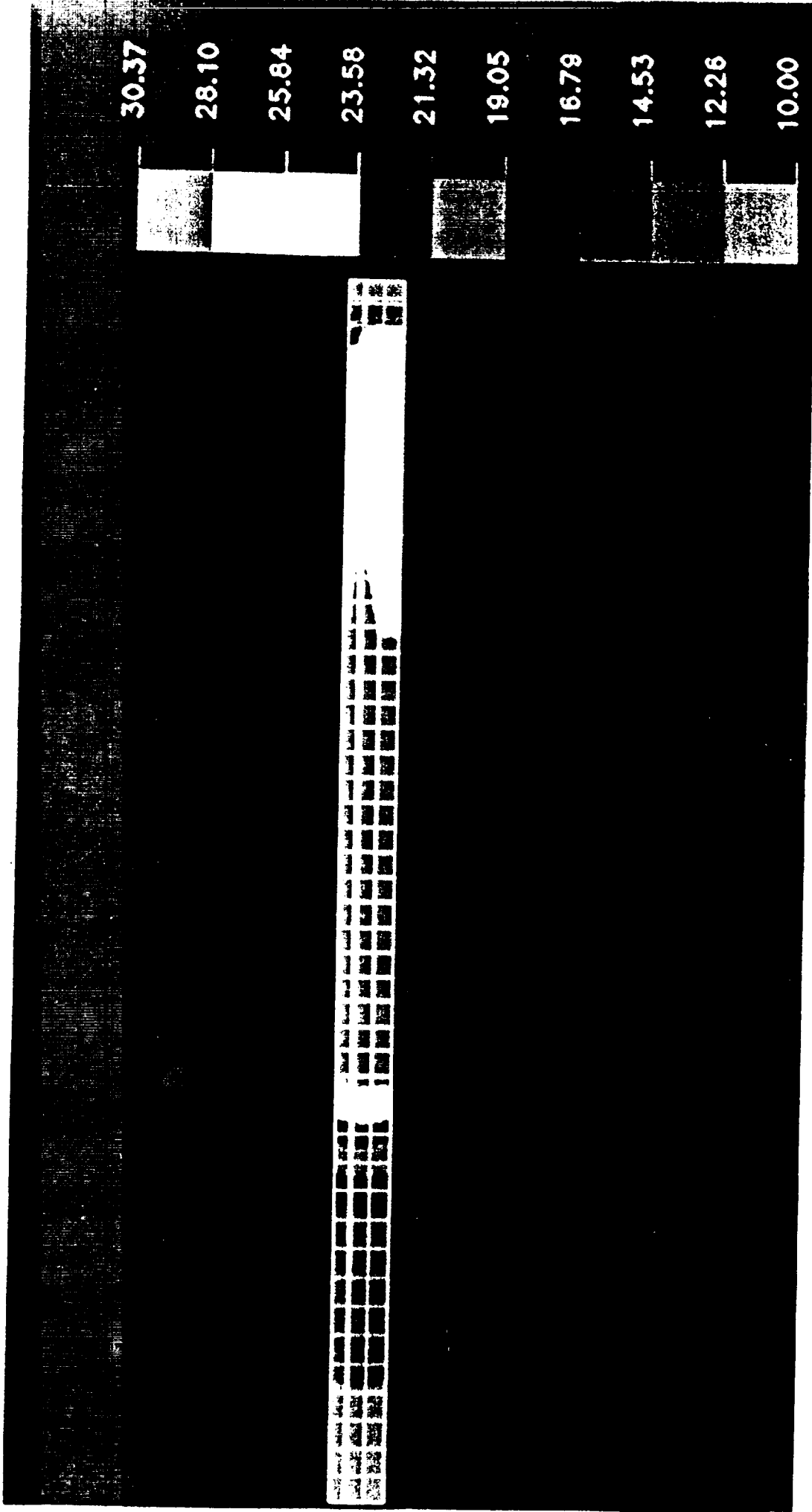


FIGURE 7. TEMPERATURE CONTOURS IN THE STACK

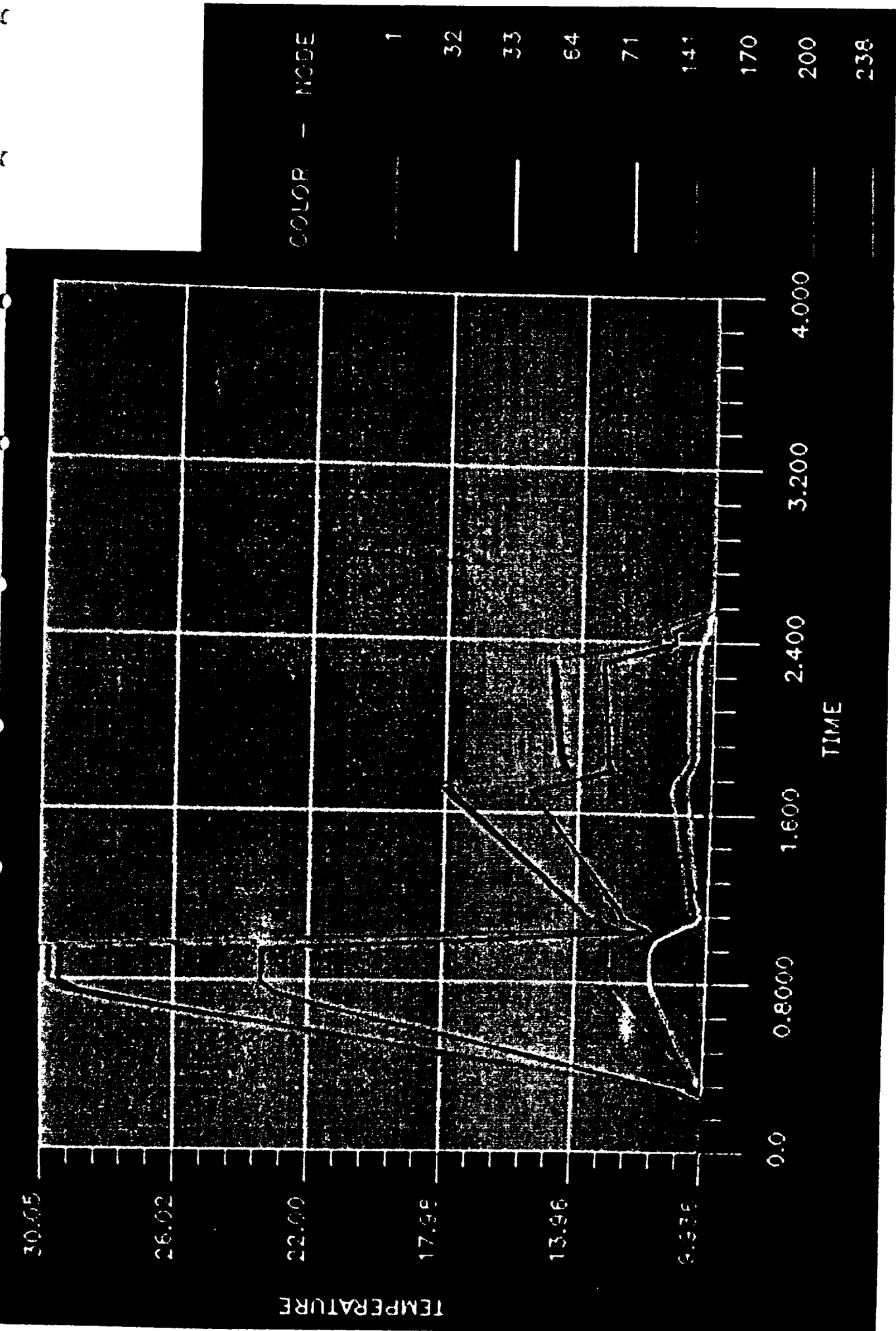


FIGURE 8. TEMPERATURE PROFILE

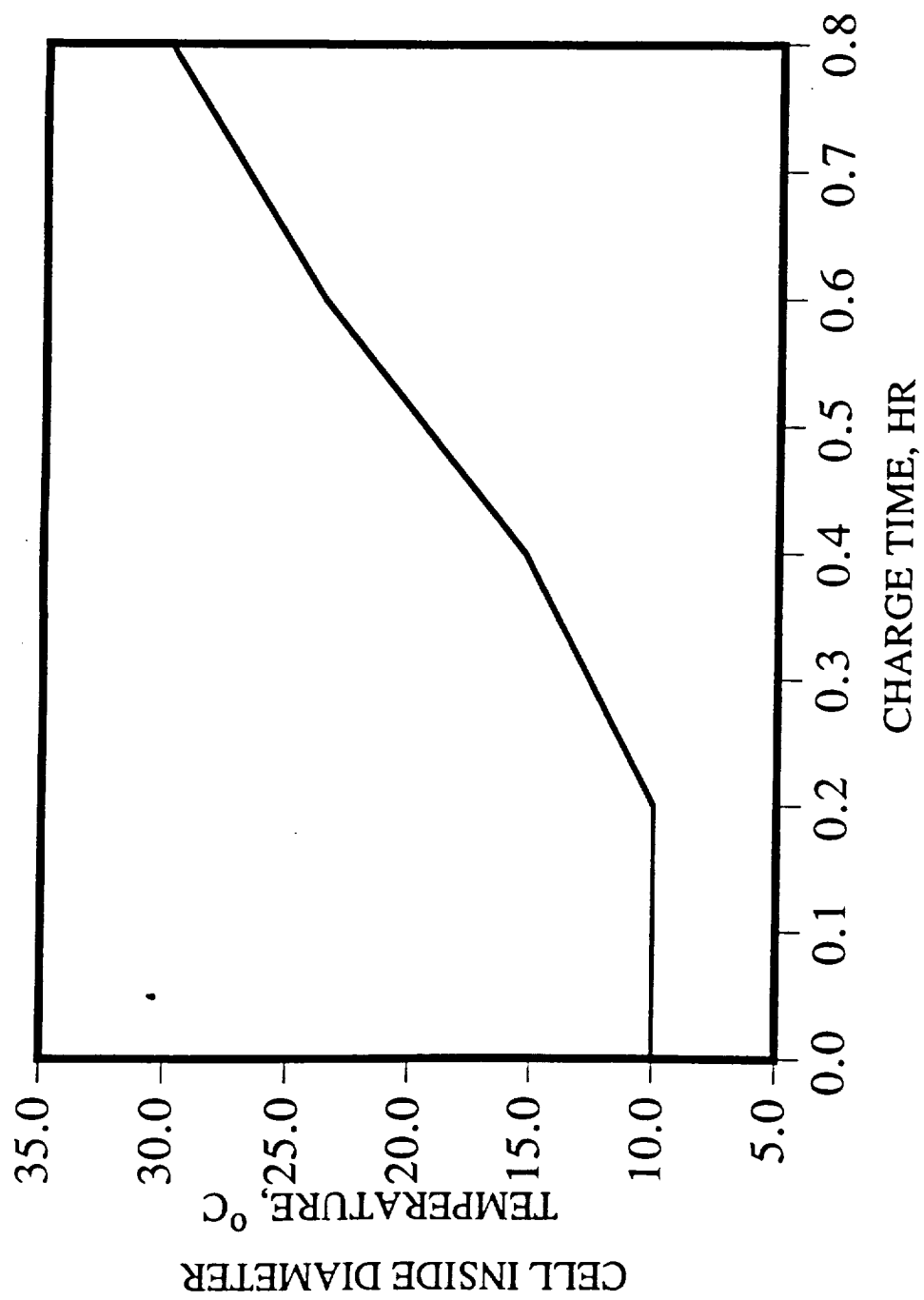


FIGURE 9. NICKEL ELECTRODE TEMPERATURE

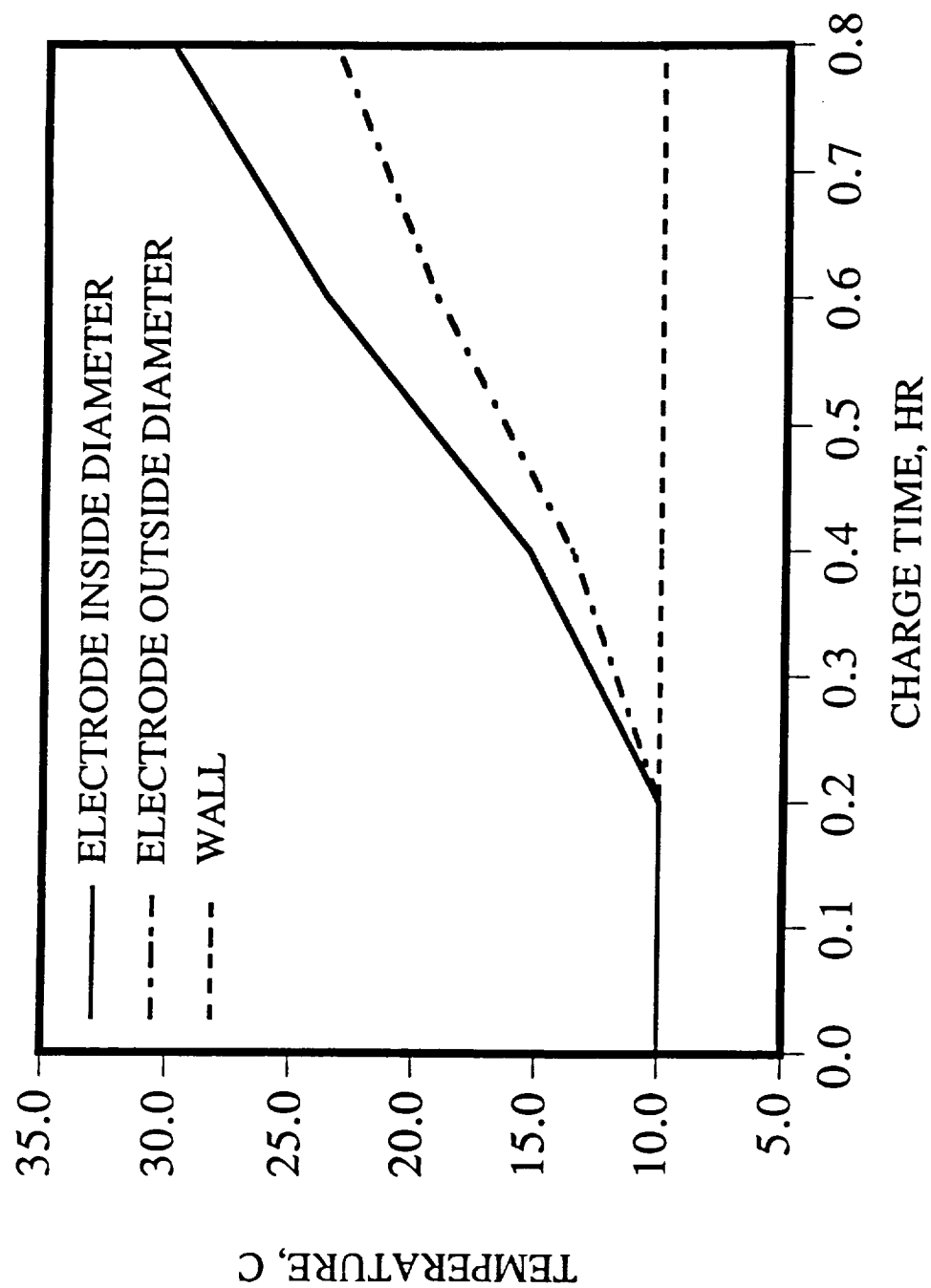


FIGURE 10. TEMPERATURE PROFILE OF AIR FORCE DESIGN

REFERENCES

- [1] Puester N., "Phase I Value Engineering Study Resulting in Increased Producibility of Air Force Ni-H₂ Design," Proc. 17th Intersociety Energy Conversion Engineering Conference, 786-789, 1982.
- [2] Lynn Marcoux, "High Energy Density Rechargeable Battery for Satellite Applications," AFWAL-TR-83-2065, 1983.
- [3] Smithrick, J.J., "Effect of LEO Cycling at Shallow Depths of Discharge on MANTECH IPV Nickel Hydrogen Cells," Proc. 23th Intersociety Energy Conversion Engineering Conference, 447-451, 1988.
- [4] Hartjen, G.L., et al., "Storage and Testing of 220 AHr Nickel Hydrogen Battery Cells in Low Earth Orbit," Proc. 23th Intersociety Energy Conversion Engineering Conference, 363-366, 1988.
- [5] Adler, E., et al., "Nickel Hydrogen Battery Advanced Development Program Status Report," Proc. 15th Intersociety Energy Conversion Engineering Conference, 1891-1896, 1980.
- [6] Kerr, R.L., "Oxygen Generation and Recombination in Nickel Hydrogen Cells," 130-147.
- [7] Gonzalez-Sanabria, O.D., "Effect of NASA Advanced Designs on Thermal Behavior of Ni-H₂ Cells," Proc. 23th Intersociety Energy Conversion Engineering Conference, 453-456, 1988.

- [8] Thaller, L.H., et al., "Design principles for Nickel Hydrogen Cells and Batteries," Proc. 20th Intersociety Energy Conversion Engineering Conference, 1.145-1.150, 1985.
- [9] Kerr, R.L., "Heat Generation in Nickel Hydrogen Cells," Proc. 21th Intersociety Energy Conversion Engineering Conference, 1521-1526, 1986.
- [10] Rogers, H.H., et al., "Failure Mechanisms in Nickel Hydrogen Cells," AFAPL-TR-77-90, 1977.